

Advanced Materials for Nickel—Metal Hydride Chemical Power Sources

Alexei Volodin, Boris Tarasov and Dmitry Blinov

ABSTRACT

A general survey on Ni-MH power sources is given, their advantages and disadvantages are shown, and the reported experimental data for improving their performance are summarized. The prospect of using carbon nanostructures to improve the performance of electrodes is considered and the effectiveness of their use is shown. The resulting materials can be used to produce electrodes for Ni-MH batteries and metal hydride fuel cells.

INTRODUCTION

Nickel-metal hydride (Ni-MH) alkaline power sources occupy one of the leading positions in the market due to their high energy density, cyclic stability, and good environmental compatibility [1, 2]. In terms of energy storage capacity and cyclic stability, Ni-MH sources are inferior only to lithium-ion (Li-Ion) batteries, and in terms of safety in operation, they significantly exceed the latter. The efficiency of a metal hydride power source is affected by the composition of cathode and anode materials, the method of preparing electrodes, the contact density between the active electrode material and the current collector, the diffusion of hydrogen in the volume of a metal hydride, the chemical and physical nature of the electrolyte, etc. In order to improve the performance of Ni-MH power sources a complex modification of the anode, cathode and electrolyte compositions can be used, as well as promising new materials able to increase electrical conductivity, to ensure good contact of the electrodes and high kinetics of charge-discharge processes.

Alexei Volodin, Boris Tarasov, Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 1, Semenov Avenue, Chernogolovka, 142432, Russia
Dmitry Blinov, Joint Institute for High Temperatures of the Russian Academy of Sciences, 13 Bd.2, Izhorskaya Street, Moscow, 125412, Russia

ALKALINE POWER SOURCES

Alkaline power sources got their name from the electrolyte used in them. In most cases, it is an aqueous solution of potassium or sodium hydroxide. Among the alkaline power sources of the second kind (rechargeable batteries) and fuel cells, the most common elements are the ones with nickel as the cathode and a transition or rare-earth metal or polymetallic alloy as the anode (Ni-Fe, Ni-Zn, Ni-Cd, Ni-MH) [2, 3]. Here Ni-MH batteries are of particular interest since they have a high density of stored energy and good cyclic stability. Besides metal hydride fuel cells do not use platinum and are capable of operating at low temperatures. The capacity of different type batteries is shown in Figure 1.

In modern Ni-MH batteries, the anode consists of polymetallic alloys containing rare earth metals, and $\text{Ni}(\text{OH})_2/\text{NiOOH}$ is used as a cathode [1–4]. During discharge hydrogen from the hydride interacts with the hydroxide ion of the electrolyte to form H_2O , and on the positive electrode, H_2O reacts with NiOOH to form $\text{Ni}(\text{OH})_2$ and OH^- . During charging the reverse reactions take place. Thus, the reactions occurring in the battery represent the movement of hydrogen from one electrode to the other. Ni-MH batteries are more expensive than Ni-Cd, but they have 30% more capacity and do not have a memory effect.

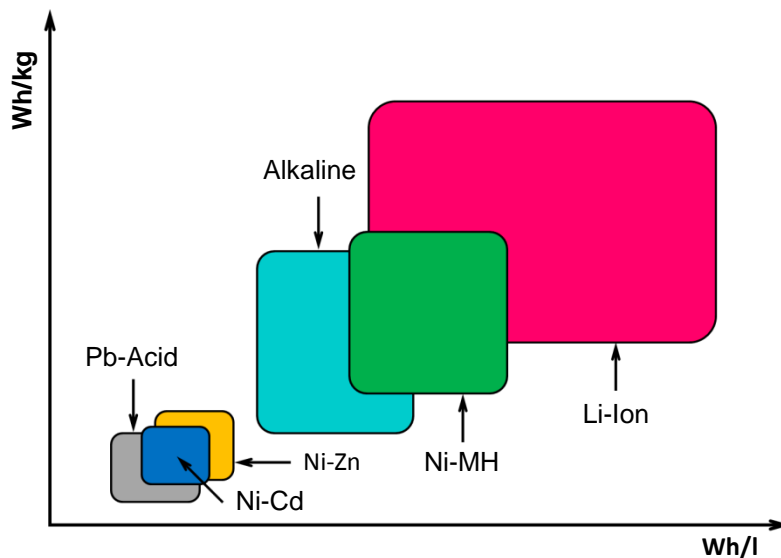


Figure 1. Energy storage capability of common rechargeable battery systems.

ANODE MATERIALS

At present, AB₅-type alloys are actively used as working materials for Ni-MH power sources. The hydrogen capacity of the LaNi₅H_{6.6} hydride is ~ 1.4 wt.% [5], and the current sources based on Co-doped LaNi₅ reach ~ 350 mAh/g in capacity [6]. In order to increase the capacity, the alloys are usually alloyed with lighter elements, such as magnesium. It is impossible to directly introduce magnesium in the composition of LaNi₅, therefore, AB₃-, A₂B₇- and A₅B₁₉-type alloys are used [7]. It is also possible to improve the electrochemical parameters by combining two or more rare-earth metals (La, Ce, Nd, Pr). For example, the introduction of neodymium into the alloy can increase the resistance to oxidation, increase the exchange rate of the hydrogen reaction, as well as the rate of diffusion of hydrogen in the alloy [8]. One of the key problems in the work of anode materials is the delivery of electrons to the collector. Whereas a pure metal or intermetallic alloy has metallic conductivity, their hydrides are dielectrics. For example, the electrical conductivity of pure magnesium is 2.27×10^7 S/cm, and its hydride (MgH₂) is $10^{-18} \dots 10^{-12}$ S/cm.

CATHODE MATERIALS

Ni(OH)₂ is used as the cathode material in all alkaline nickel-based power sources due to its low cost, good performance and wide operating temperature range. The specific energy capacity of the cathode part (~ 290 mAh/g) is provided by the β-form of Ni(OH)₂. The performance of α-Ni(OH)₂ is somewhat better, but this phase is extremely unstable. To stabilize α-Ni(OH)₂, a partial substitution of nickel ions in the hydroxide lattice by cobalt ions [9] or aluminum [10] is used. In the latest work, it was shown that the addition of 7 mol.% Al to Ni(OH)₂ leads to an improvement in the reversibility of the reaction, a decrease in the electrochemical resistance, an increase in the specific capacity and cyclic stability. However, as in the case of anode materials, one of the key tasks remains the charge transfer process. β-Ni(OH)₂ has a very weak electronic conductivity ($10^{-14} \dots 10^{-8}$ S/cm) due to a large distance between neighboring Ni atoms ($d_{\text{Ni-Ni}} = 3.12 \text{ \AA}$). Shorter Ni–Ni bonds (2.86 Å) of NiOOH favor a better overlap of the orbitals and higher electrical conductivity (0.01...0.05 S/cm), but this value also does not allow achieving the desired result.

COMPOSITE MATERIALS

Acetylene soot or graphite (G) is usually added to anodic and cathodic materials to improve electrical conductivity. However, as a result of side reactions (first of all, oxygen evolution at the cathode), soot oxidizes rather quickly, especially at high charge-discharge current densities. In addition, to achieve high conductivity, it is necessary to introduce these additives in large quantities, which reduces the specific capacity of the electrodes, and a small amount does not lead to the desired effect. When forming electrodes, powders of intermetallic compounds or Ni(OH)₂ are pressed with various additives on the collector. Such a preparation procedure can lead to a decrease in the efficiency of active materials due to poor contact between the active particles and the current collector. The inclusion of additional binding materials, such as polytetrafluoroethylene, which is a dielectric, also reduces the specific capacity of the electrodes.

The use of extended carbon nanostructures (CNS) such as Graphene-like material (GLM), carbon nanotubes (CNT) and carbon nanofibers (CNF), as alternatives to acetylene soot and graphite, is of particular interest. Composites of anodic and cathodic materials have been obtained earlier by mixing the active components with graphene-like materials [11]. In [12], multi-walled nanotubes were grown on the surface of electrode materials from nickel foam. The resulting electrode capacity was 360 mAh/g, which is 18% higher than the electrode capacitance without nanotubes. The authors of [13] grew Ni(OH)₂ crystals on the surface of a graphene-like material. Such composite materials not only improve charge transfer, but also reduce internal resistance. However, studies of this kind are sporadic and need to be developed systematically in order to achieve an optimal result.

In our studies [14, 15], it was noted that the addition of 3 wt.% of carbon nanotubes and nanofibers to titanium or lanthanum oxides leads to a significant increase in conductivity. Composites based on nickel hydroxide were also formed: G/Ni(OH)₂, CNT/Ni(OH)₂, CNF/Ni(OH)₂, and GLM/Ni(OH)₂ containing 3 wt.% of the carbon component. It is shown (Figure 2a) that the addition of graphite to Ni(OH)₂ increases the electrical conductivity from 3.7×10^{-9} to 1.33×10^{-7} S/cm; CNT – to 3.9×10^{-3} S/cm; CNF – to 6.8×10^{-3} S/cm; GLM – to 8.9×10^{-2} S/cm. The calculated volume fractions of carbon nanostructures in the composites were CNT – 6.2 vol.%; CNF – 7.1 vol.%; GLM – 6.7 vol.%. The obtained composites were used as materials for the electrodes of Ni-MH cells. Their electrochemical characteristics are studied. Preliminary results demonstrate the performance of composite electrodes in the composition of Ni-MH power sources. The addition of CNTs increases the capacity from 102 mAh/g (for pure hydroxide) to 265 mAh/g, the addition of nanofibers to 223 mAh/g, and graphene-like material to 195 mAh/g (Figure 2b).

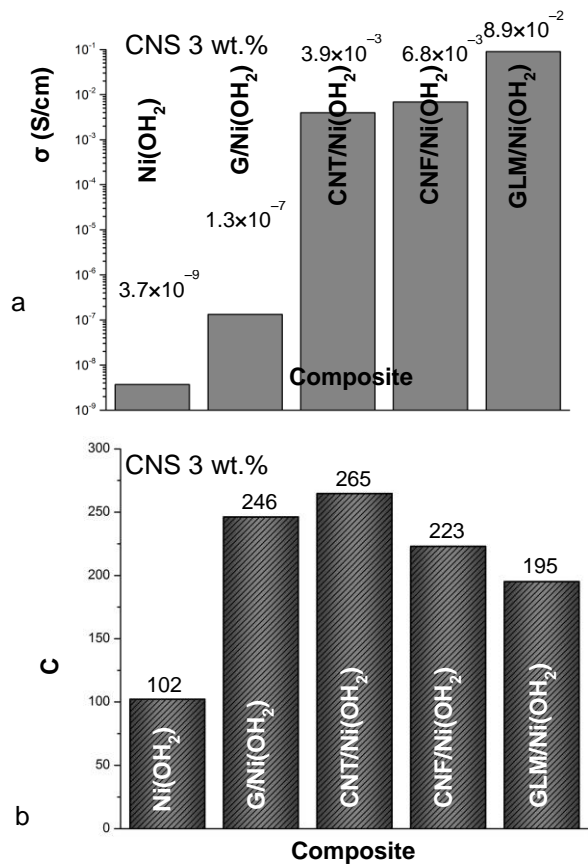


Figure 2. Electrochemical characteristics of electrode materials: a) Specific conductivity of composites; b) Specific capacity of the composite electrodes.

CONCLUSION

One of the key problems in the operation of anode and cathode materials is the delivery of electrons from active electrode materials to the collector. To achieve high conductivity, it is necessary to introduce acetylene soot or graphite additives in large quantities, which reduces the specific capacity of the electrodes, and a small amount does not lead to the desired effect. The addition of 3 wt.% carbon nanostructures (CNT, CNF, PMG) can increase the electrical conductivity of the electrode materials more than seven orders of magnitude. Composite electrodes exhibit high performance, oxidation resistance and good cyclic stability. The resulting materials can be used to produce electrodes for Ni-MH batteries and metal hydride fuel cells.

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REFERENCES

1. Winter, M., and R.J. Brodd. 2004. "What are batteries, fuel cells, and supercapacitors?" *Chem. Rev.*, 104(10):4245-4269.
2. Hannan, M.A., M.M. Hoque, A. Mohamed, and A. Ayob. 2017. "Review of energy storage systems for electric vehicle applications: Issues and challenges," *Renew. Sust. Energ. Rev.* 69:771-789.
3. Ovshinsky, S.R., M.A. Fetcenko, and J. Ross. 1993. "A nickel metal hydride battery for electric vehicles," *Science*. 260:176-181.
4. Yartys, V., D. Noreus, and M. Latroche. 2016. "Metal hydrides as negative electrode for Ni-MH batteries," *Appl. Phys. A.*, 122:43.
5. Liu, W., and K.F. Aguey-Zinsou. 2016. "Low temperature synthesis of LaNi₅ for hydrogen storage," *Int. J. Hydrogen Energy.*, 41:1679-1687.
6. Zhou, W., D. Zhu, Z. Tang, C. Wu, L. Huang, Z. Ma, and Y. Chen. 2017. "Improvement in low-temperature and instantaneous high-rate output performance of Al-free AB₅-type hydrogen storage alloy for negative electrode in Ni/MH battery: Effect of thermodynamic and kinetic regulation via partial Mn substituting," *J. Power Sources.*, 343:11-21.
7. Hu, W.K., R.V. Denys, C.C. Nwakwuo, T. Holm, J.P. Maehlen, J.K. Solberg, and V.A. Yartys. 2013. "Annealing effect on phase composition and electrochemical properties of the Co-free La₂MgNi₉ anode for Ni-metal hydride batteries," *Electrochim. Acta.*, 96:27-33.
8. Volodin, A.A., Ch. Wan, R.V. Denys, G.A. Tsirlina, B.P. Tarasov, M. Fichtner, U. Ulmer, C.C. Nwakwuo, and V.A. Yartys. 2016. "Phase-structural transformations in a metal hydride battery anode La_{1.5}Nd_{0.5}MgNi₉ alloy and its electrochemical performance," *Int. J. Hydrogen Energy*, 41:9954-9967.
9. Guo, D., E. Shangguan, J. Li, T. Zhao, Q. Li, X.Z. Yuan, and H. Wang. 2014. "Effects of γ -CoOOH coating on the high-temperature and high-rate performances of spherical nickel hydroxide electrodes," *Int. J. Hydrogen Energy.*, 39:3895-3903.
10. Huang, J., D. Cao, T. Lei, S. Yang, X. Zhou, P. Xu, and G. Wang. 2013. "Structural and electrochemical performance of Al-substituted β -Ni(OH)₂ nanosheets electrodes for nickel metal hydride battery," *Electrochim. Acta.*, 111:713-719.
11. Lin, J., C. Lu, Z. Cao, and L. Wang. 2016. "Ti-V-Ni with graphene-mixing icosahedral quasicrystalline composites: Preparation, structure and its application in Ni-MH rechargeable batteries," *Int. J. Hydrogen Energy.*, 41:1098-1103.
12. Xie, F., C. Dong, W. Qian, Y. Zhai, L. Li, and D. Li. 2015. "Electrochemical properties of nickel-metal hydride battery based on directly grown multiwalled carbon nanotubes," *Int. J. Hydrogen Energy*, 40:8935-8940.
13. Wang, H., H.S. Casalongue, Y. Liang, and H. Dai. 2010. "Ni(OH)₂ Nanoplates grown on graphene as advanced electrochemical pseudocapacitor materials," *J. Am. Chem. Soc.*, 132:7472-7477.

14. Volodin, A.A., A.A. Belmesov, V.B. Murzin, P.V. Fursikov, A.D. Zolotarev, and B.P. Tarasov. 2013. "Electro-conductive composites based on titania and carbon nanotubes," *Inorg. Mater.*, 49(7):656-662.
15. Volodin, A.A., P.V. Fursikov, A.A. Belmesov, Yu.M. Shulga, I.I. Khodos, M.N. Abdusalyamova, and B.P. Tarasov. 2014. "Electrical conductivity of lanthanum oxide based composites containing carbon nanofibers," *Inorg. Mater.*, 50(7):673-681.